Reactivity

of

Ontario and North Carolina Phosphates

A Summary

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Both iron and phosphate, if they occur separately in the environment, can be the source of serious environmental problems. But since they have a strong chemical affinity for each other they normally tend to keep each other in check. Since iron is one of the major drivers of acid generation many studies have explored the possibility of mixing various phosphate products, such as commercially-available fertilizer or dissolved phosphate salts, with acid generating mine wastes to reduce or even eliminate acid mine drainage In general, the studies have concluded that although phosphate inhibits AMD, that high material and application costs make it economically impractical.

Since 1992 Boojum Research Limited has been conducting large scale field trials in which it has applied natural phosphate rock (NPR), a granular waste product of phosphate mines operated by Texas Gulf in North Carolina, to acid-generating mine wastes. These trials have demonstrated not only that phosphate works, but that it can provide an extremely economical solution to AMD. The trials have shown not only that phosphate is effective in lower application rates than proposed by other workers, but that it is effective when simply scattered onto tailings deposits, waste rock piles, or acid-impacted lake sediments as opposed to previous suggestions that it must be mechanically mixed into the waste. Since the material cost of NPR is negligible the only major expenditure associated with its use, is shipping. Accordingly, laboratory tests conducted by Boojum to determine the specific chemical behaviour of the Texas Gulf North Carolina NPR, were enlarged to include NPR from mines in Ontario.

Laboratory experiments were carried out to compare leaching from various phosphate rock materials in distilled water (mimics rain) and sulphuric acid slurries mimics conditions in tailings/waste rock pile. Materials were exposed to several short decant cycles over a period of weeks. Materials tested were from North Carolina (Code 31, Code 38), Spanish River (Spanish River Carbonatite) and Kapuskasing (Agrium Tailings, Agrium High Grade, Low Fe Residuum Ore). The aim of the experiment was to compare the suitability of the materials for use in various situations on the mine site to inhibit the generation of acidic drainage.

The main points of this study were:

- Slurries of ratio 1:5 and 1:10 (weight: volume) were made with distilled water, simulating rain, to define the initial leaching characteristics.
- Slurries of 1:10 were made with 0.1N H_2SO_4. Decant cycles, of short time intervals were used to reduce the effect of the reduction of dissolution due to saturation in the supernatant (Table 1). These conditions can be related to the acidic pore water of mine tailings. The decantation process was continued until the neutralisation capacity of the materials was exhausted (8 cycles).

- In the natural phosphate material, the phosphate minerals are not equally distributed. If the particle size can be related to phosphate content and to its release, then through selecting the suitable particle size fraction of the material, the costs for shipping the material for the sought application in acid generating tailings could be greatly reduced..

- The Spanish River material produced the highest pH in distilled water, suggesting that the carbonate component in this material is very soluble (Table 2). The Agrium High Grade Low Fe ore is acidic, with a low pH of 3.18 and released substantial acidity (344 mg $CaCO_3$/L one hour after set-up) in distilled water. Both North Carolina products and the Agrium tailings range in pH from 8.5 to 7.4 higher then the distilled water used with a pH value of 6.2.

- The Code 48 and the Spanish River Carbonatite gave the greatest release of cations in the sulphuric acid slurries, reflected in the largest reductions of the electrical conductivity (EC) values (Table 3). On the other hand, Agrium tailings did not release a large quantity of cations in sulphuric acid. Code 31, the fine ground phosphate with the high surface area, has cations available over longer periods. EC values hardly changed from decant cycle 0 to 7. Overall, the EC observations suggest that the initial release of elements is rapid, reflecting first order kinetics, which is followed by a gradual release and formation of salts, such as calcium sulphate.

- All materials tested reduced the acidity of the sulphuric acid slurries (Table 4). The smallest reductions were found with the Agrium mine materials. The reduction of acidity was greater with the North Carolina materials, particularly Code 31. The reductions were much more consistent through the 8 decant cycles with Code 31 than with the other materials. Alkalinity release was most rapid but short-lived for the Spanish River material. This characteristic is relevant to the longevity of the inhibition or reduction of acid generation observed in the use of the North Carolina material on tailings and in waste rock, as the acid generation process is a gradual one, and through the anticipated precipitation of Fe^{3+} which takes place above pH 3, the acid generating process rate is reduced.
- The titrations with NaOH indicate that the materials from Agrium and the North Carolina deposit are very different (Figures 1-3). It is likely that the differences are related to Fe^{3+} and Al^{3+} content. The Spanish River material has a high neutralizing capacity, as it contains 65 % calcite as $CaCO_3$ which increased the pH and subsequently no other elements were released. This certainly does not make it suitable for the intended application of acid mine drainage in sulphitic waste material, as it essentially functions like limestone. Phosphate is not released in an elevated pH environment and thus is not available to precipitate the Fe^{3+}, a reaction that is considered most important.
- The lowest release of phosphate in the sulphuric acid slurries is associated with the Spanish River Carbonatite which only started to release phosphate after Decant Cycle 4 and then, only at a minimal rate compared to that of other rocks (Table 5). The phosphate release of Code 31 was very consistent with the intended application in sulphitic wastes, releasing a steady amount with each decant cycle. Both Agrium materials released phosphate at a rate similar to the Code 48 material. Code 31 showed the best performance both with respect to acidity reduction and phosphate release.
- The elemental composition of the Ontario materials (Table 6) differs from the North Carolina products with respect to their higher iron content. So there may be reason to use it cautiously, depending on the relative amount of iron in the

mine wastes to be treated. The North Carolina materials differ also from the Ontario materials with their lower barium, manganese and titanium concentrations. However these differences are not important, given that the application rates would make those elements likely undetectable.

Overall Assessment of materials in terms of neutralising capacity and P release in relation to suitability of these materials in mining operations:

Spanish River Carbonatite. Is very "reactive" in acid conditions and neutralises acid very quickly. It has by far the highest neutralising capacity of the materials tested. However the phosphorus content is relatively low (1.41 %) and only 4.9 % was released during the course of the acid leachings. It is essentially like a limestone with a high P content.

Texus Gulf (Code 31 and Code 48). These materials have a high P content. Code 31 has an effective and long-lived neutralising capacity and also released more and a higher % of its P content during the experiment. Code 48 showed erratic behaviour through the decant cycles.

The ***Agrium*** materials were acidic (reaction with distilled water) but also had acid neutralising capacity. They were less effective in neutralising the acid than the North Carolina materials. In terms of neutralising capacity, there was little difference between the two materials. Both released similar amounts of P under acidic conditions than the North Carolina Code 48 but less than Code 31. The Agrium materials, particularly the Agrium tailings have a high Fe content which must be borne in mind when specific applications are considered. Precipitation of Fe oxyhydroxides around the phosphate material may reduce further dissolution.

Overall, in terms of neutralising capacity and P release, Code 31 could be considered the most effective of the tested materials in the experimental conditions. Code 48 and the Agrium materials may provide longer-term effectiveness in a field situation. Spanish River Carbonatite neutralises very rapidly whereas P release is delayed and limited in quantity.

Table 1: Volume Added (mL) to 10 g material and reaction time (h) for decant cycles

Decant Cycle	Volume	Stirring Time	Settling Time	Total Reaction Time	Cumulative Time
Sulphuric Acid (0.1 N, pH 1.4)					
0	100	0.02	1.0	1.02	1.02
1	100	0.5	0.5	1.00	2.02
2	100	1.7	16.0	17.7	19.68
3	100	0.5	0.5	1.00	20.68
4	200	1.0	2.0	3.00	23.68
5	100	1.0	16.4	17.4	41.05
6	100	0.5	1.5	2.00	43.05
7	100	0.5	1.0	1.50	44.55
8	200	0.42	642.8	643.2	687.7
Total	1100	6.10	681.6	687.7	687.7
Distilled Water					
9	300	1.00	2.0	3.00	3.00
10, day 0	300	21.0	2.0	23.0	26.0
10, day 62	-	-	1486.5	1486.5	1486.5
Total	600	22	1490.5	1512.5	1515.5

Table 2: Slurries 1:5 and 1:10 (solid:liquid) with distilled water day 0, day 30, day 62

NPR and Distilled Water (control)	pH			Conductivity (uS/cm)			Acidity (mg L^{-1})			Alkalinity (mg L^{-1})			Eh (mV)			Phosphorous (mg L^{-1})		
	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62
	Slurry 1:5 ratio (20 g solid: 100 ml liquid)																	
Agrium Tailings	7.44	6.92	-	121	345	-	6.6	37.8	-	14.5	65.2	-	702	407	-	1.58	0.111	-
Spanish River Carbonatite	8.73	7.23	-	102	132	-	1.5	24.7	-	47.2	57.5	-	548	416	-	0.011	0.057	-
Agrium High grade Low Fe Residuum Ore	3.18	3.63	-	1200	1560	-	344	274	-	-	-	-	693	644	-	2.23	0.08	-
Texasgulf Phosfil (Code 48)	8.53	6.70	-	174	665	-	-	54.4	-	22.9	41.3	-	562	466	-	1.42	0.04	-
Precipitate With Phosphate, PWP (Code 31)	8.09	7.04	-	500	833	-	-	46.8	-	57.6	88.5	-	491	470	-	1.52	0.785	-
	Slurry 1:10 ratio (10 g solid: 100 ml liquid)																	
Agrium Tailings	6.49	7.45	7.73	93	281	355	14.9	32	27	5.8	48.1	45.3	454	348	359	1.06	0.07	0.10
Spanish River Carbonatite	8.79	7.26	8.15	64	118	131	8.6	15.5	8.6	38.8	72.3	57.1	386	356	353	0.011	0.01	0.01
Agrium High grade Low Fe Residuum Ore	3.03	3.07	2.76	1114	1821	2880	380	339	514	-	-	-	621	659	716	1.55	0.34	0.35
Texasgulf Phosfil (Code 48)	7.44	7.53	7.52	85	465	610	7	16.2	13.2	16.9	45.2	43	499	352	530	1.00	0.05	0.08
Precipitate With Phosphate, PWP (Code 31)	7.56	7.38	7.77	288	624	681	12.7	16	14.1	39.4	64.6	53.1	430	331	513	1.20	0.88	0.74
Distilled H_2O		6.16			23			8.2			7.1			448			0.015	

Table 3: Measured electrical conductivity (µS/cm) for decant cycles 0-10

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residuum Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid (0.1 N, pH 1.4, EC 37,800 µS/cm)					
0	19110	5250	32300	13170	6980
1	10820	3690	13800	6030	5500
2	8300	2730	9360	4040	4160
3	18020	3230	17110	31900	4850
4	17680	2710	12160	14030	4490
5	12160	2750	14710	6590	4300
6	19090	10020	31800	18750	4510
7	16550	11220	33000	31200	6700
8	7670	2980	6350	2650	3180
Distilled Water					
9	950	1693	1117	1435	1883
10, day 0	938	1704	1010	740	1742
10, day 62	1294	1752	1960	1775	1800

Table 4: Acidity measured (mg L^{-1}) for decant cycles 0-10

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residuum Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid (0.1 N, pH 1.4)					
0	4945	487	4943	3378	2719
1	4250	229	4652	2248	2723
2	3634	73	3795	1814	2279
3	4848	417	4809	4494	2979
4	4751	113	4437	3894	2805
5	4251	218	4384	2863	2722
6	4867	2364	4778	4477	2872
7	4864	4504	4759	4537	2818
8	3993	1236	3795	1872	2928
Distilled Water					
9	50.2	99.6	157.9	44.5	583.3
10, day 0	36.4	54.4	45.9	45.6	176.4
10, day 62	45.2	68.5	142.3	14.7	195.9

Figure 1: Titration Curves, Decant Cycle 1

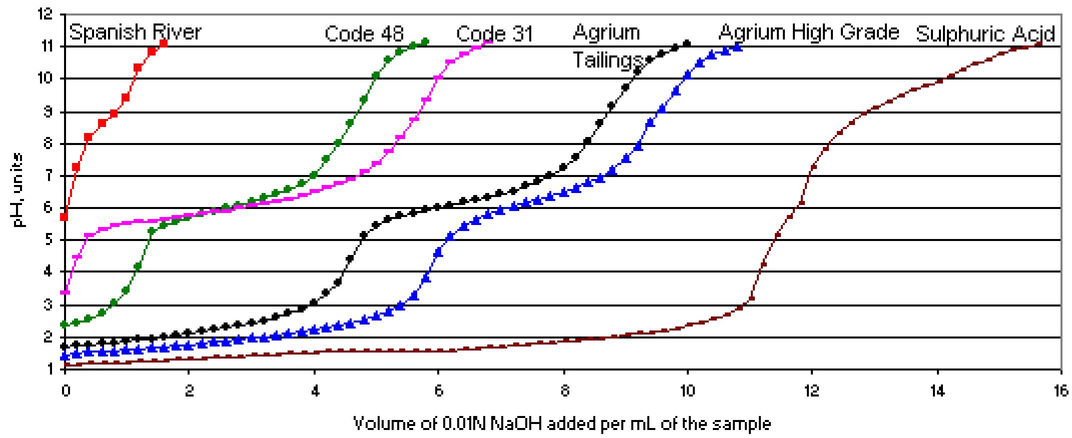

Figure 2: Titration Curves, Decant Cycle 8

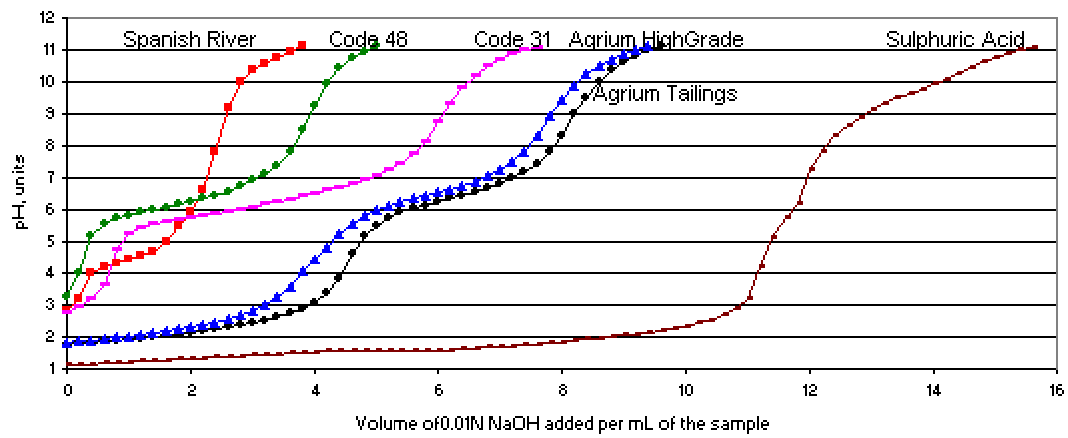

Figure 3: Titration Curves, 1L, 10g, 46 days

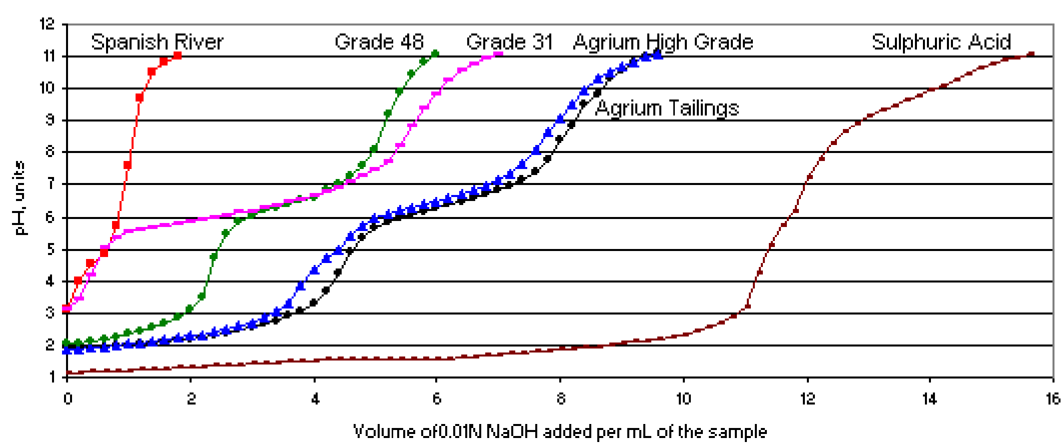

Table 5: Phosphorus (mg L^{-1}) released over decant cycles 0-10

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residuum Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid (0.1 N, pH 1.4)					
0	58	0.059	118	189	473
1	358	0.189	324	341	659
2	582	0.011	613	502	686
3	255	0.18	321	127	713
4	269	0.41	563	273	767
5	509	1.03	413	536	629
6	223	1.29	215	184	890
7	232	1.5	163	152	706
8	536	2.14	613	544	949
Distilled Water					
9	2.7	0.03	20	3.1	107
10, day 0	1.8	0.03	4.6	2.6	30
10, day 62	2.7	0.01	3.6	0.52	8.1

Table 6: Elemental composition of phosphate materials

Element	Code 31	Code 30	Code 30	Code 31	Code 48	Code 48a	Code 48b	Code 48 (White)	Code 48 (Gray)	Agrium Tailings	Spanish River	Agrium High Grade
Major Elements (%)												
Al	0.21	0.20	0.20	0.24	0.29	0.55	0.97	0.22	0.41	0.28	1.48	1.38
Ca	31.1	33.1	33.4	35.2	32.3	31.1	17.8	30.7	27.6	27.5	22.2	25.6
Fe	0.33	0.32	0.36	0.39	0.49	0.67	12.7	0.42	0.78	12.50	4.34	4.43
K	0.08	0.08	0.11	0.11	0.15	0.16	0.14	0.11	0.19	0.02	0.77	0.01
Mg	0.31	0.32	0.28	0.32	0.48	0.32	0.21	0.39	0.26	0.09	1.05	0.16
Na	0.69	0.76	0.75	0.78	0.55	0.58	0.32	0.43	0.69	0.15	0.34	0.13
P	12.1	12.8	12.3	13.3	7.96	8.92	9.04	6.13	9.97	11.2	1.41	9.38
S	1.06	1.03	1.21	1.22	0.95	1.22	0.00	0.65	1.13	0.20	0.05	2.45
Sr	0.23	0.26	0.24	0.26	0.20	0.19	0.10	0.17	0.20	0.28	0.30	0.33
Minor Elements (µg/g)												
Ba	38	41	38	46	31	34	33.7	28.8	46	260	400	390
B	872	824	851	842	310	364	32.6	94.8	1030	360	40	82
Cd	39	38	44	43	2	5	22.1	5.9	8.7	8.2	0.9	2.5
Co	-1	-1	-1	-1	-1	-1	-0.3	0.6	1.2	83	12	140
Cr	117	128	125	139	53	58	90.6	52.7	81.2	19	-0.5	98
Cu	7	8	9	10	3	99	365	7.2	9.7	17	18	64
Mn	13	12	41	20	17	74	121	12.2	10.9	1780	880	610
Ni	13	15	17	16	8	13	4.1	11.1	19.5	34	0.9	94
Pb	-3	-3	-3	-3	-3	-3	-1	-1	-1	35	4	25
Ti	52	12	35	33	44	47	93.5	60.5	88.3	400	1880	100
V	18	20	20	22	19	20	29.4	18	24.5	350	51	380
Zn	307	308	341	337	63	1320	2330	73.1	97.1	260	59	340